Organic Photochemistry and Pericyclic Reactions
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Module No. # 01
Lecture No. # 27
Cycloaddition Reaction-1

In the, for the last 4 classes, we were discussing about sigma tropic reactions under pericyclic subject, right. Sigma tropic reactions, what we saw in sigma tropic reaction is that we saw 1, sigma tropic reactions can be broadly classified as 1, n sigma tropic reactions and n, n sigma tropic reactions. Under 1, n sigma tropic reactions, we were studying about 1 3 1 5 1 7 hydrogen shifts. Then, we started studying about 1 3 1 5 1 7 carbon shifts and then, we studied about how this hydrogen or the metal group should move, whether it is suprafacial movement or anterafacial movement and we used our Woodward Hoffmann rule for deciding that.

After finishing this 1, n sigma tropic reaction, then we slowly went into n, m sigma tropic reactions, where we studied how a sigma bond can be moved to the pie system and in n, m sigma tropic reactions, we then studied 2, 3 sigma tropic and 3, 3 sigma tropic reactions. In 2, 3 sigma tropic reactions, we studied on many reactions like Stevenson's (( )) acyl rearrangement and we covered many of the reactions. Then, in 3, 3 we slowly studied about your cope rearrangement, we studied all the aspects of cope, right. How cope reactions steroid chemistries, we studied about them then, we studied about oxycope, then we slowly went into their azacope systems and we did some examples on cope rearrangement.

After finishing cope rearrangement, then we went into claisen rearrangement and we studied there synthetic utility of claisen rearrangement. We studied different variance of claisen rearrangement like your Johnson claisen rearrangement, Harland claisen rearrangement and we studied some aromatic claisen rearrangement. Then, we finally, we ended up with studying 5, 5 sigma tropic rearrangements and 9, 9 sigma tropic rearrangements.

So, that is about the one important class of pericyclic reactions, that is your sigma tropic reactions. So, from today’s class, we will be trying to focus on cycloaddition reactions. This is another set of reaction which is broadly comes under your pericyclic reactions.

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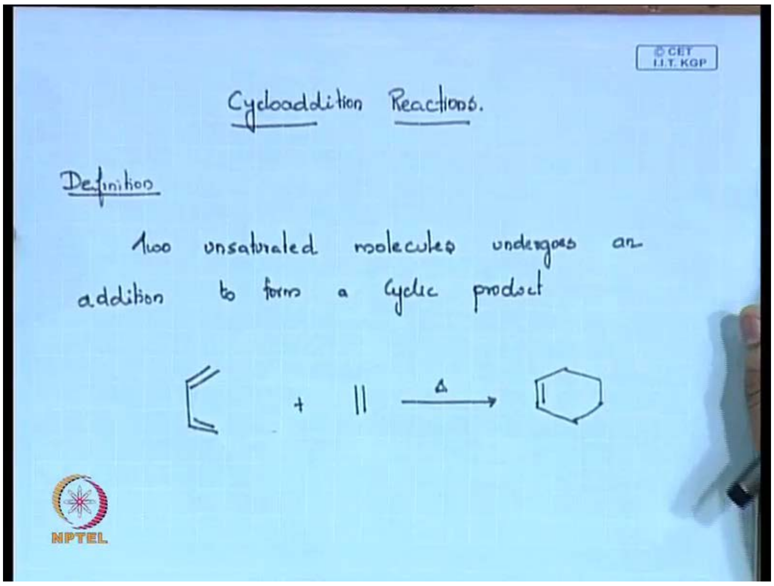

Cycloaddition Reactions.

Definition

Two unsaturated molecules undergoes an addition to form a cyclic product

So, we will try to spend like another 2 or 3 class on understanding about cycloaddition reactions. So, the broad definition if you want to know about, it is like two unsaturated molecules, two unsaturated molecules undergoes an addition to form a cyclic product. This is your cycloaddition reactions. The best one is that you take an unsaturated system like your dye and another unsaturated molecule is your alkene. If you heat this reaction, it forms a type of cyclic product. So, this is a class, a broad class definition of your cycloaddition reaction like two unsaturated molecules undergoes an addition to form a cyclic product, but there are many reactions in which you can see even three molecules or four molecules under go in cycloaddition type of reactions, but it is a broad definition, simple definition we can keep like two unsaturated molecules undergoing an addition to form a cyclic product. So, this is a definition about cycloaddition reactions.

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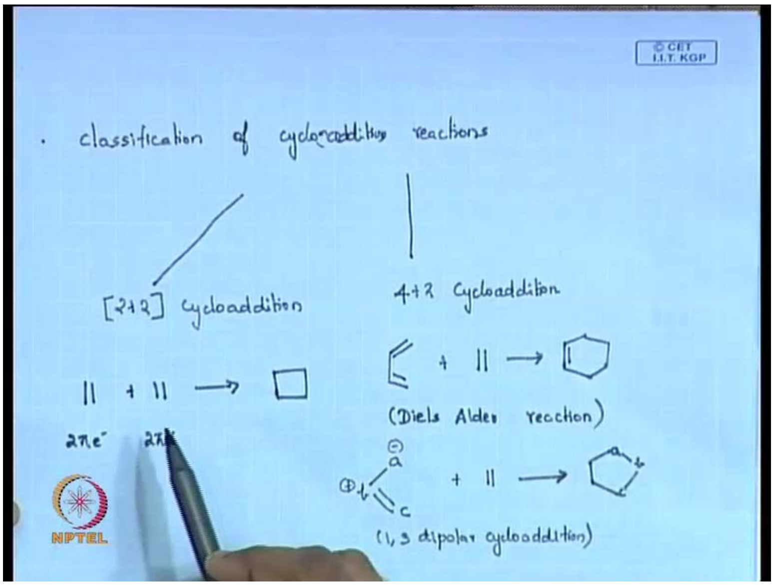

The another thing is classification of cycloaddition reactions. How we can classify cycloaddition reactions? Based on number of pie electrons that is involved in your reactions. Based on that, we can classify your cycloaddition reactions, fine. For example, like we can classify them as 2 plus 2, very important classification of cycloaddition, 2 plus 2 cycloaddition where you can think an alkene reacting with another alkene to form a cyclobutane system.

Here you can see, it is two pie electrons and same way, it is two pie electrons adding together to form cyclobutane system. This is 2 plus 2 cycloaddition and then, we can even think about your 4 plus 2 cycloaddition, where you can have your butadiene plus your alkene to give you a cyclic product. So, this will be a 5 4 pie electron system and this will be your 2 pie electron system. So, giving you a cyclic product, this is your famous reaction, this is your Diels alder reaction. Then, we have like we can even have a system like this, where you have a, b and your c with your (( )) a. Again, if you see this is four electron system, where you have two electrons here and have two electrons here. So, it is a four electron system with your alkene to give you a five member ring. This you can call as you have studied this 1 3 dipolar cycloaddition have this reaction. Same way you can write 4 plus 4 cycloaddition reactions.

So, basically how you classify cycloaddition reaction is that you classify cycloaddition reaction based on number of pie electrons interacts in the system. So, in the earlier case, you have seen like 2 pie electrons and 2 pie electrons interact to give you a cyclobutane system. That is why we call it as 2 plus 2 cycloaddition. In Diels alder, we can see 4 pie electrons and 2 pie electrons. So, it is more like a 4 plus 2 cycloaddition. Clear? So, that is how you can classify the cycloaddition reactions.

Now, before getting into understanding like 2 plus 2 cycloaddition and 4 plus 2 cycloaddition reactions, what we will do is that we will try to understand more about the mode of additions. So, what we will be trying to focus in this coming classes is that we will work on 2 plus 2 cycloaddition reactions. Then, we will study 4 plus 2 cycloaddition in which we will be concentrating more on diels alder reactions and 1 3 dipolar cycloaddition. These are three reactions we will be concentrating for the coming class.

So, now, we will just see the mode of addition how the cycloaddition reaction happen based on your FMO projection, like (( )) molecular orbital how we can understand the mode of action.

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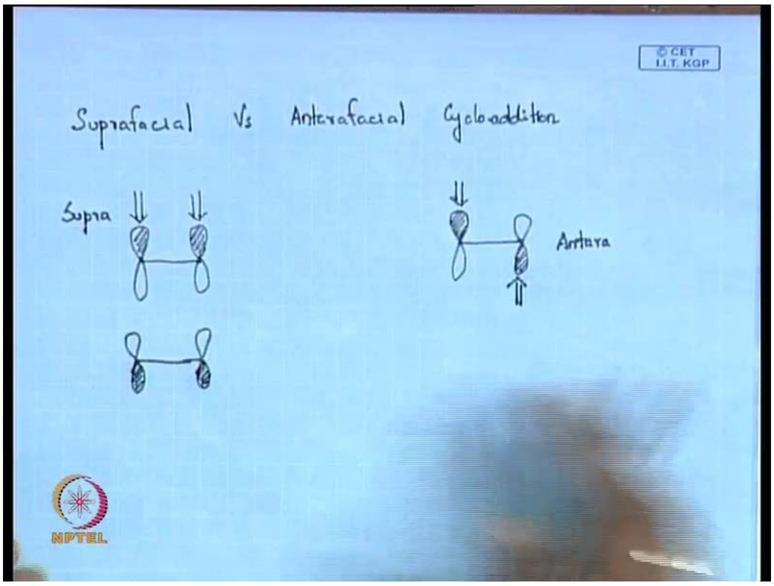

So, basically we call them as a suprafacial verses anterafacial cycloaddition. So, what this suprafacial and anterafacial means exactly? For example, I am taking a system like, see I am taking a molecular orbital. I am taking a molecular orbital like this, right. Now, in the case, I have system where I have like this.

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Now, if during the addition, the homolumo which we are talking about the home of one of the reaction and lumo of another reaction which we are going to talk about, if this addition happens exactly on the symmetry lobe, that is, on the same side phase, then we call this as supra. If our addition takes place in opposite one, then we call this as an antera, right. So, if it is in the same phase, the same phase of your orbital with the homolumo, then you call it as suprafacial. If it is on one on the suprafacial and another is opposite to it, then you call that addition as an anterafacial addition.

Much more to be very precise for example, I will consider them now. For example, I am taking a system. This is not an alkene type of system like just we say that it is an n system or just a minute, much more to be clearly drawn.

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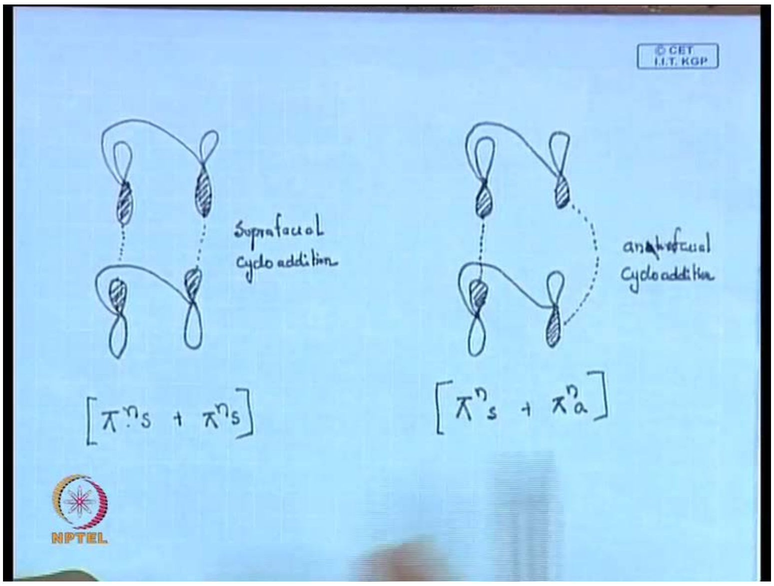

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Have a system like this. Just to show that it is not a single, it is an end and this can be n number of carbons in between occurs just to give that idea. So, now, you see this cycloaddition, the homo and lumo. The one is homo, another is the lumo. You see they are happening in the same phase and that we call as suprafacial cycloaddition. So, how we call this? We can just say that this is pie. We normally call as we can put your two or n because this is n system. So, I can keep it as pie n s plus another pie n s system, ok.

If it is two electron systems, then you make it 2 pie 2 s plus pie 2 s or pie 4 s plus pie 2 s. This is your suprafacial because it happens in the same thing. If we go and see how anterafacial addition will be, orbital homo of one if you see in this case what happens is you can have one on their symmetrical, right same size, but other case, we will have in the opposite. So, that will be anterafacial. So, this will be suprafacial and this will be anterafacial. So, how you write that? You write as pie n s plus pie n a, right. So, this is your addition. So, normally we call as anterafacial cycloaddition.

This is pie n s plus pie n a, because this is anterafacial and this is suprafacial. In this case, both are suprafacial. This is like a general step then we can slowly, so, that is how you call cycloaddition. You can say the system undergoes a suprafacial cycloaddition or anterafacial cycloaddition. They can have pie n s plus pie n s. Both are suprafacial. You call them as a suprafacial system. One suprafacial and another, you call as pie n s plus pie n a sent point depending on the things, right. So, this is the mode of cycloaddition based on your FMO theory.

Now, what we will do is that now we will slowly get into our 2 plus 2 cycloaddition. That is your first cycloaddition which you are going to this is just an introduction. So, what is cycloaddition? How you can classify cycloaddition? So, cycloadditions are nothing, but it is just an addition of your unsaturated molecules to form cyclic products. Classification, you can classify based on the number of pie electrons involved in the system. Then, we have seen the suprafacial and anterafacial, same symmetrical, same phase lobes. Then, you call as supra. It is just opposite to say and try to say upon anterafacial and how to name them? Pie n s plus depending upon your pie system. What number? It is 2 electron systems. Then, you say pie 2, then whether this suprafacial or anterafacial.

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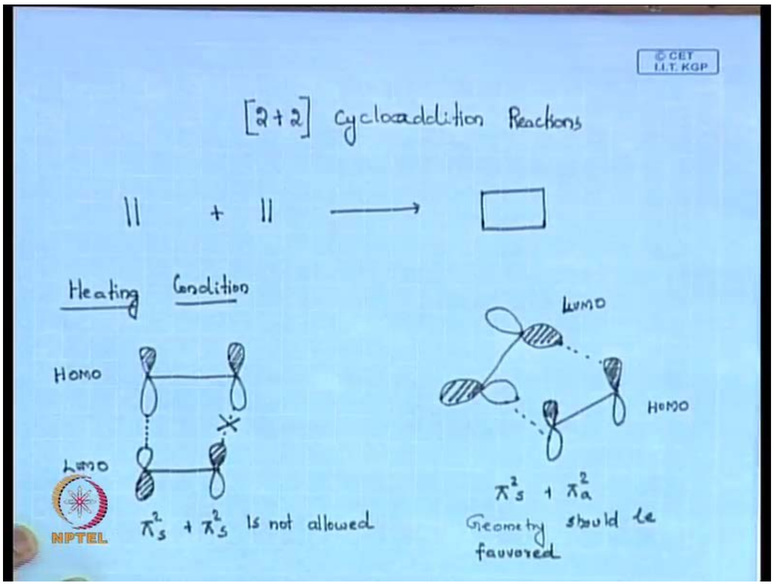

So, that is an introduction about your cycloaddition reactions. Now, we will get into your 2 plus 2 cycloaddition reactions.

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We have studied that if you take 2 alkenes, I am not just specifying any congestion right now. Just we combine to give you a type of cyclic product. You call these reactions as 2 plus 2 cyclic addition reaction. Now, we will see under what condition, how this happens if you thermally activate this reaction, whether it will undergo or whether it is allowed. If it is allowed, then what happens? So, it is suprafacial cycloaddition or it is an anterafacial. Whether it is pie 2 s plus pie 2 s or it is pie 2 a on photo chemical activation. What will occur? So, first we will try to understand that and then, we will go and see the examples.

So, we will see in heating. What you can see in heating condition? That is all thermal activation how the orbits look because we know it is 2 plus 2. For example, we can take your alkene system. So, we will draw the homo of your one of your alkene and then, we will take the lumo of another alkene system, right. We can take another alkene system also. Now, because this should be in the heating condition, right, this is the homo of your one of your alkene and this is your lumo.

Whether they can do now a system, I can have this, but this is not allowed. So, what we can say is that pie 2 s plus pie 2 s is not allowed in heating condition. It is not allowed. So, you cannot have this. See most of the time if it is suprafacial, it is the reactions are much more allowed. It can go nicely. You have seen very rare examples, where you can have suprafacial and anterafacial, those type of reactions are there, but if it is supra suprafacial, it is much allowed reactions.

A supra anterafacial one of the problem is that they have to be geometrically allowed. That condition prevails. We will say we will take the same example. If I want to do, if you want to draw like a suprafacial and anterafacial for this type of system, so this is the homo of your alkene, this is your homo.

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For example, I am considering like that and this is your lumo. So, now, you can always have a chance of if it geometrically favors. So, you have a chance of making like this, right. Then, you can say this is pie 2 s plus pie 2 a. So, if you generalize this, like you can say that heating condition cycloaddition reactions does not undergo your suprafacial, it is not allowed, but you can think about undergoing suprafacial plus anterafacial reaction, but the char here is that it should be geometrically favored. If it is not geometrically favored, then this alignment of your suprafacial to anterafacial never takes place. So, most of the case, they become forbidden unless the geometry allows them. That is the important thing you have to remember. The geometry should be possible, some geometry should be favored. Otherwise, you cannot see all this. This is on your ET.

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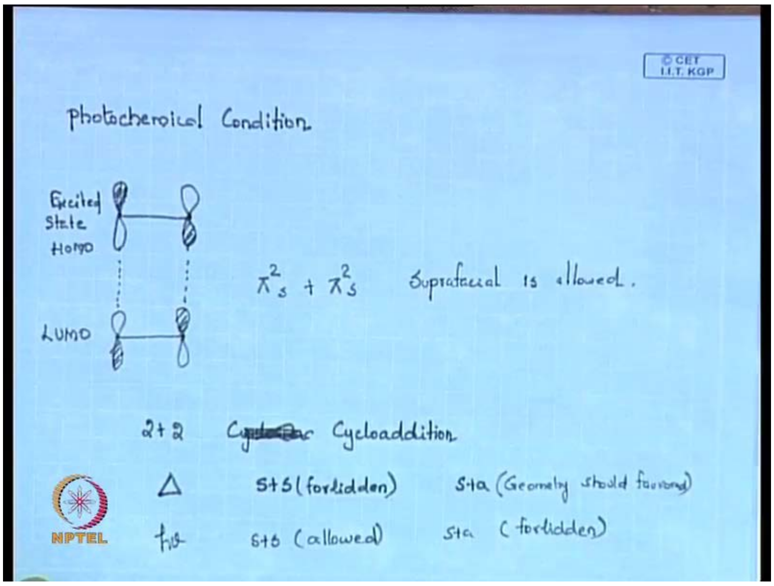

Photochemical Condition

$\pi^2_s + \pi^2_s$ Suprafacial is allowed.

2+2 Cycloaddition

Δ s+s (forbidden) s+a (Geometry should favour)

$h\nu$ s+s (allowed) s+a (forbidden)

What will happen if I fertilize this under photo chemical condition? So, same way we can write now under photo chemical condition you can. So, what happens you will write now excited state homo, right because you are exciting the one of alkenes. So, you will be writing excited state homo and you will be writing your lumo of your alkene, another system. Previous case, you are thinking about the ground state. Now, since it is photo chemical, you are exciting. So, you are generating a new type of homo and new homo that you call as an excited state homo and now you are writing about the lumo.

Now, in this case, you can see the orbitals are aligned nicely to form a pie 2 s plus pie 2 s which is suprafacial, right. So, what we can say then? If we do 2 plus 2 cycloaddition, so if you heat it, your s plus a is completely forbidden, right. You can then say s plus s is completely forbidden when you heat, but you can see s plus a, but it should be geometry should favor, but if you shine light s plus s is allowed, you can have s plus a is not forbidden.

So, like that you can finally generalize based on your FMO3 like heating what happens here is s plus s forbidden s plus a is allowed geometrically if it is favored. Then, in light s plus s is allowed and s plus a is forbidden. Clear?

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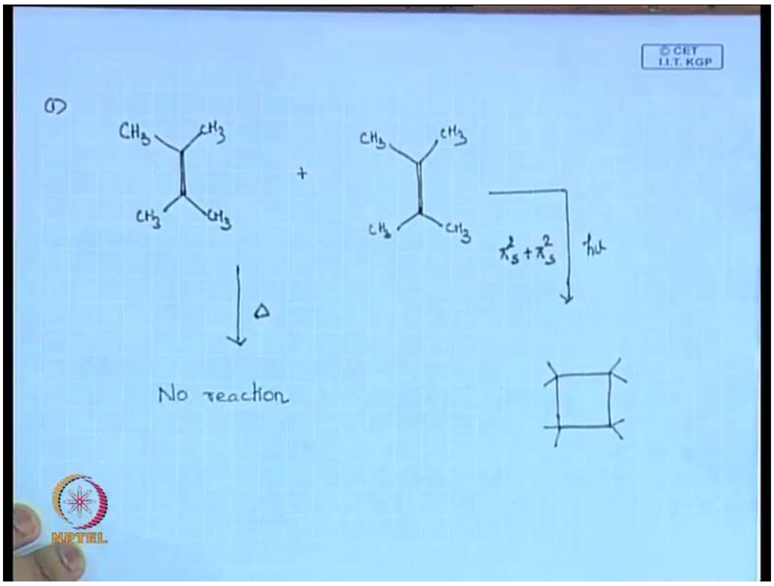

So, that is about introduction of your 2 plus 2 cycloaddition reactions. Now, we will just get into some examples and see whether we can use this idea. We will take the simplest example like we will take your alkene system like dine system and other same dine.

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So, if you fertilize this reaction, if you excite this, what you end up? Yes, first we write the product. So, you end up with a cyclic product like this, right. So, how this reaction is, what mode of addition it should be? Supra supra, right. So, we should call them as pie 2 s plus pie 2 s, right. See that is very important because you have to, once we go to systems where you can generate your chiral carbon, then you should know whether the reaction is specific or not.

That time your supra supra facial additions are very important. In this case fine, but we will go for some other examples where we can see that why pie 2 s plus pie 2 s is important. Same way if I heat this reaction, what you expect? See what happens is that we should think about pie 2 s plus pie 2 a should be a supra facial anterafacial because you do not have this pie 2 s plus pie 2 s is forbidden heating. So, it should be pie 2 s plus pie 2 s a, but if you see this alkene system, they are more same. They are not geometrically favored. It cannot sit on each other like this. So, geometry does not allow. That is why what happens, there will be no reaction. So, you will have no reactions. It is a very good example to understand. So, it should, but basically we should think about pie

2 s plus pie 2 a, but the idea is that since the geometry is small for them, so it is easy to make a bond. It does not happen. So, you get, there will be no reaction, but if you do the same reactions in light, you get a nice product ok.

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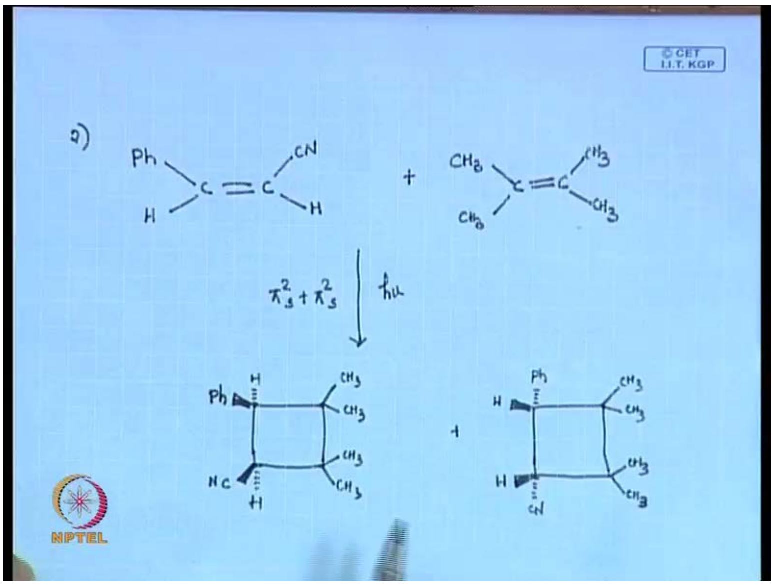

Now, we will take the second example.

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Now, what I am doing is that now sort of when you do a cycloaddition on this, you will generate a type of chiral carbon, right. Now, you should know how your systems if I fertilize this, first thing comes into your mind is that it should be supra supra, right. So, it should be pie 2 s plus pie 2 s. So, it should be the same phase. It should come in the same phase. Then, how your product should be if I write the product this is one side of my alkene. That is my metal. I have my metal here and this is my alkene part and this is my phenol part which I am going to write.

So, it should be most of the time you get my phenol here, get my hydrogen in one side and I can get my c n here with my hydrogen on 0.5, right. You get a type of specific product or it can be other way round. If you can say that it is, I can get in like CH3, CH, right then, also think about this first. So, this tells the reaction is proper and comes in the phase to make a bond. So, you are not changing any steroid chemistry here because you get very nice products. If it is like the trans, you get in the same type of product here. If you take trans amide end up, then with two different minds. That is good.

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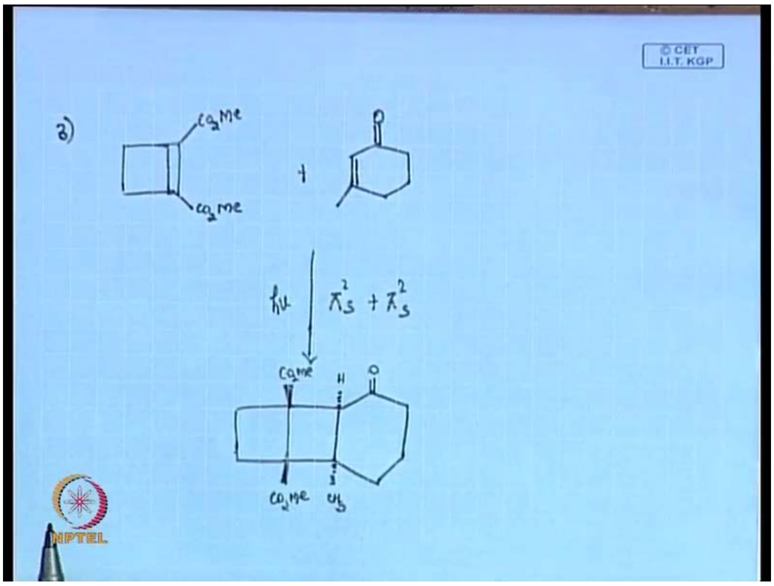

Same way, we will take one another example. This is third one.

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Just a case your alkenes type of alpha beta (()), so you can have your 2 plus 2 cycloaddition here. So, this reaction once you fertilize, you can write pie 2 s plus pie 2 s. So, you want to have a steroid chemistry because it comes in the same phase of that. So, 2 CO 2 should be, yes you can then write. First, we will finish the product. Co2me and you have a co2me, then you have your hydrogen and you have your metal, right. So, this is another important, another type of example which tells about suprafacial how it should be very precise in additions.

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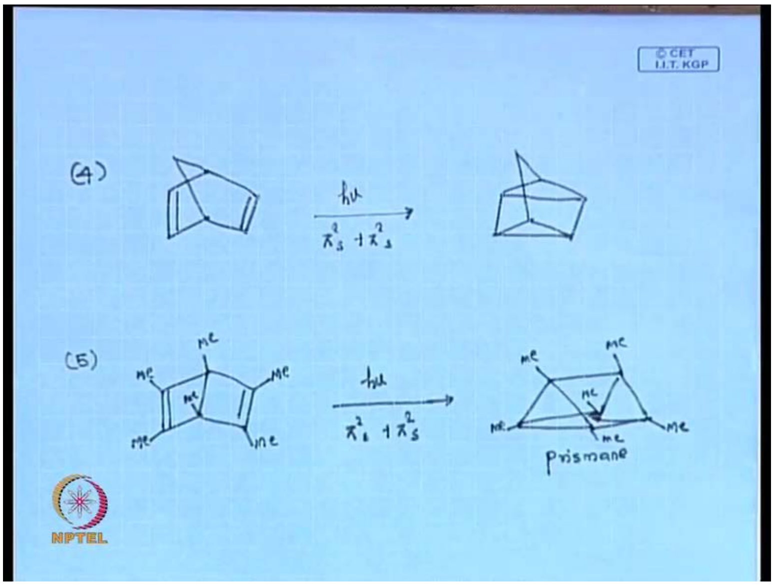

We will take some interesting examples which will be, which you guys have studied this example, right. I think we have just seen this example when we are talking about allene pie system chemistry, right. So, when we fertilize this, we can say it under goes plus pie 2 s plus pie 2 s. So, I have to draw a product nicely.

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It undergoes cartridge cyclo systems. So, another example which we will be interested of speaking about is your this, we have studied. Where we have studied this example?

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Where we have studied this type of your benzene? These are benzene types. It is a metal substitute type of your benzene and once you fertilize this, again it under goes a nice pie 2 s plus pie 2 s system. Can you draw this structure? It will be interesting to draw this structure.

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Shall I prismine type? People be like prismine. Then, you can put your orderly metals here. So, you get this type of nice reaction. So, these are very good reactions of your cycloaddition of under photo chemical conditions. Now, what we will do is that we will slowly get into your thermal activation, where you can end up with your pie 2 s plus pie 2 a system into plus 2.

So, we have studied that geometrically it should be allowed if it geometrically gets allowed, then you end up with a nice type of pie 2 s plus pie 2 a system. They are very good system or any idea what it can be? What type of 2 plus 2 cycloaddition, where you end up seeing pie 2 s plus pie 2 a? You have studied this in detail. Your ketene chemistry, ketene cycloaddition. Most of your ketene cycloadditions with alkene, ketene cycloadditions with your imine famous Staudinger equation reaction, then your ketene addition with your carbonyl compounds to form beta lactams. All these reactions goes by pie 2 s plus pie 2 a chemistry, that is pie 2 supra facial plus antera facial.

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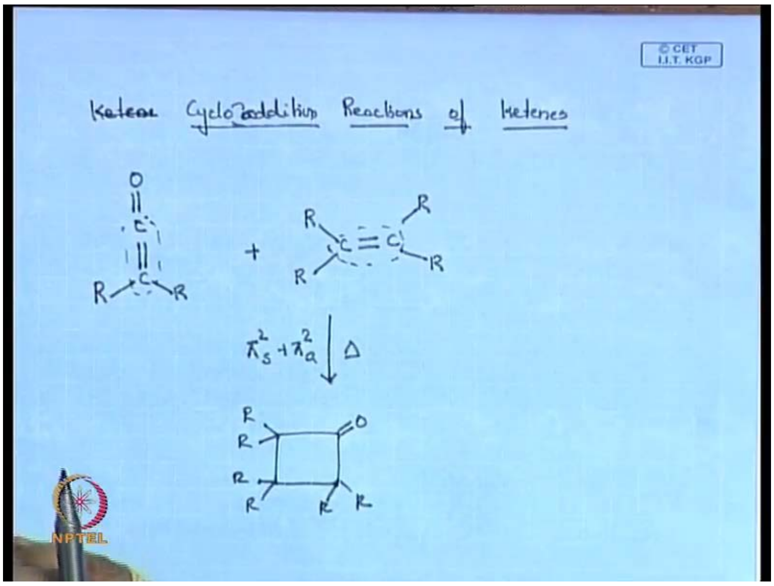

Ketene Cycloaddition Reactions of ketenes

So, what we will do is that we will study in detail ketene or I can say cycloaddition reactions of ketenes. So, we will try to understand now this in detail cycloaddition reactions of ketene. First, we will see what that reaction is all about.

You can take a step of ketene and then, you can take your alkene. For example, I am taking like a much symmetrical type of alkene and you just thermally activate this and you end up with a nice product. Yes. So, it is basically, it is a 2 plus 2 cycloaddition of your c 1 1 c and c 11 c of this and c 11. These are basically system involved that to give you the cyclic product and if you see what our rule, it says that it should be heating, means it should be pie 2 s plus pie 2 a.

Now, we will see that how the chemistry happens, how it is geometrically allowed, why it should happen this which is not happen in simple alkenes. If you take two alkenes system, it never undergo heating may no reactions, but in this case, ketene chemistry most of your reactions goes by suprafacial plus anterafacial chemistry. So, first you see why it should happen? We will see the geometry why it allows by orbital picture. For example, I am taking my alkene. You can consider the homo of your alkenes.

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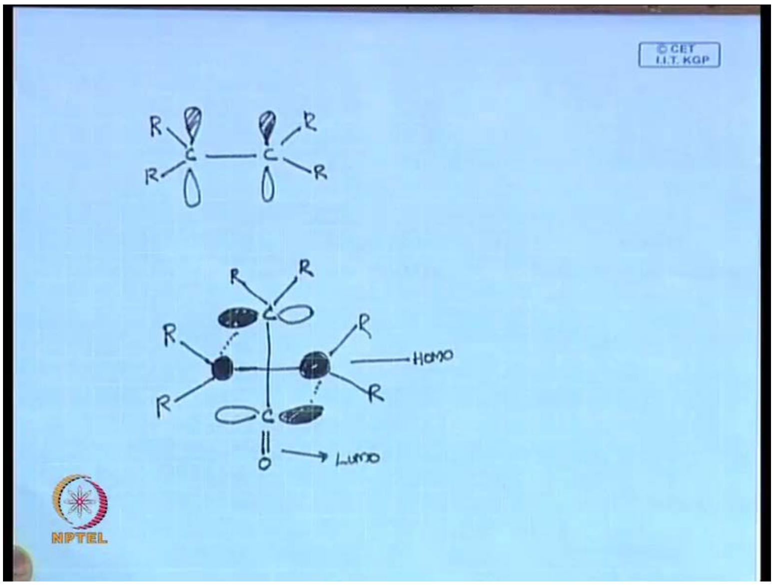

So, if you want to write I am taking this as for example, your alkene. If you want to write it big, write this type of system. What you do is that you just rotate this 90 degree, so that your loops have seen like this. So, what it is I am saying exactly, like these 2 loops which I am talking about here that you see from the top. So, is geometry his like that. So, you you see the 2 loops here. Clear? Now, what happens is that now your ketene comes and sits. The ketene which we are taking about can the carbon, we are taking about the lumo of this system. Yes, my carbon here. So, this will be the homo I am talking about. I am talking the lumo of this. So, it should be ok.

So, now the geometry is like that. So, I have an alkene, it nicely sits here. So, you can now, you can easily form a type of bonding nature system if you want or even you can write it in other way round that it should be white and white you can do it. So, it should be supra type because of sitting nature of that. It can be white here, so that you can get the white star from here and make a bond fine. So, that is why, whole geometry allows the system to do your pie 2 s plus pie 2 a chemistry. Yes, any doubt in this? Why ketene chemistry happens nicely because this geometry I am talking about.

So, what we will do is that now we will try to understand this ketene chemistry in detail. What we will do is that first we will take synthesis of heating chemistry. We will see how we can synthesize heating. Then, using our so-called homo theory knowledge, we will see how it reacts with our alkenes, how it reacts with your (()) and how it reacts with your (()). We will see that one by one. First we will see how we can synthesize ketenes. That is very important.

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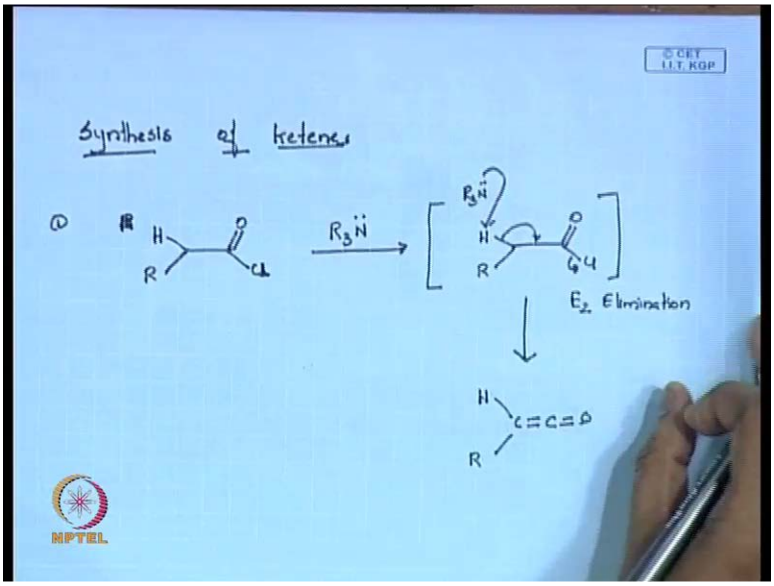

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You can know that first normal method for check synthesis of ketene. This is chloride. So, you can take this as thing acyl chloride system and use your (()) and you know what happens is that your (()), ok this can extract your hydrogen giving you a nice, you will get a nice synthesis of ketene. This one is normal synthesis of ketene. You take acyl chloride system and use base, you can get your ketene nice.

Another synthesis of your ketene is using your ester. You have studied that even same system instead of acyl chloride if you want to use like an ester type of system or same way, you can use your lithium based bases. Then, you end up with your enallied type of system O minus or O R and this type of systems, right. This can again push it back. So, it is better to know how to make ketene type of systems right because when we do synthesis, earlier case, what type of elimination it is? This one. This is your e 2 elimination, it is an e 2 elimination which happens nicely. In this case? That is more nice chemistry for what type of elimination. It is this one. This is your e 1 c b, e 1 c b elimination it can happen. So, these are nice synthesis like you can see elimination reactions much happening here.

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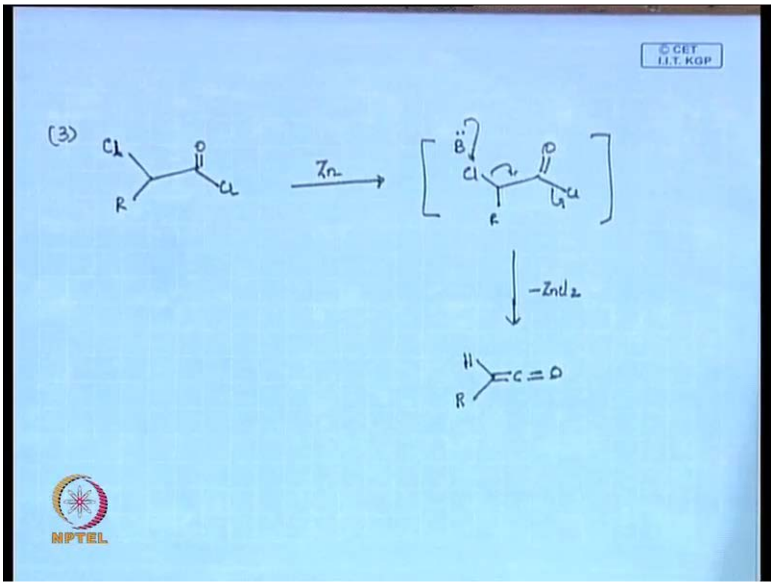

We have one more system where you can even use, even people use dychloro systems like you can have like O Chlorine systems. So, what you use because this is normally commonly used. You use this can be done in presence of zinc like, yes if you have zinc, you can do this chemistry little bit basis required for it.

If you have a, so since your zinc chloride, then you end up with your nicely. This is with you can see with the zinc type of regularly this this normally people use it, type of you have an alpha chloride system and use like metals also end up with your ketene chemistry. Another one which you have studied which on thermal activation or bi fertilizes you can generate your ketene chemistry. What is that?

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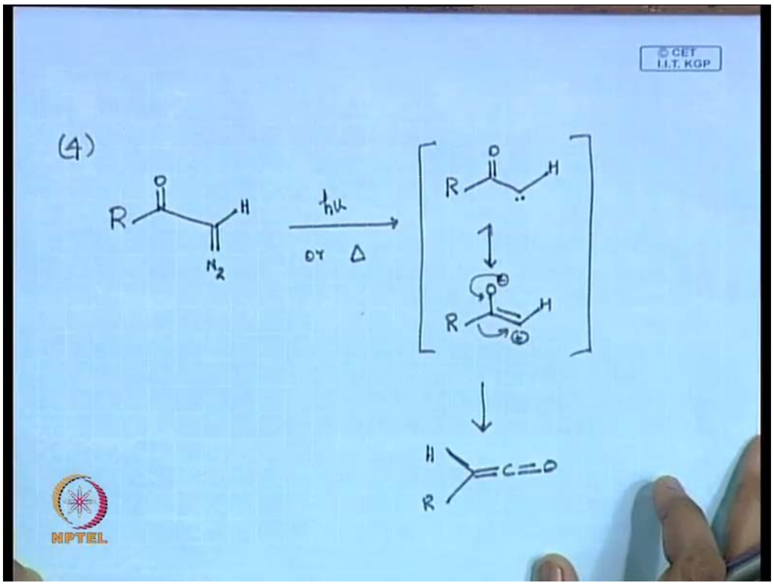

You can thermally activate and you can generate. You can end up with even the singular carbon type of systems which you have studied also. You can get your daiso systems, where you can heat it or you can thermo or you can fertilize, you end up with a carbon and then, you have 1 2 alkyl shift leading to your ketene chemistry that you have studied that in your earlier classes. Just we will write that. So, if you take this type of system if it fertilize or thermally or even if you can thermally activate this, you end up with your carbon, right or even you can say other way of writing is that R. This can be written like this also as O minus (( )) positive charge, right, so that you can end up here.

Now, it is type of rearrangement which you have studied. I have a rearrangement here, so you can think about getting your, these are four methods, other methods, but commonly used are these four methods by which you can generate your ketene. So, one we can use your acyl chlorides or you can use your esters or you can use your alpha chloro, acyl chlorides or you can think about your diazo systems where you can thermally activate or heat you end up with a ketene generations. So, these are the four methods of your ketenes.

Now, what we will do is that slowly we will understand the reactions of since, we know now synthesis of ketenes, now we will slowly get into the reactions of ketene chemistry.

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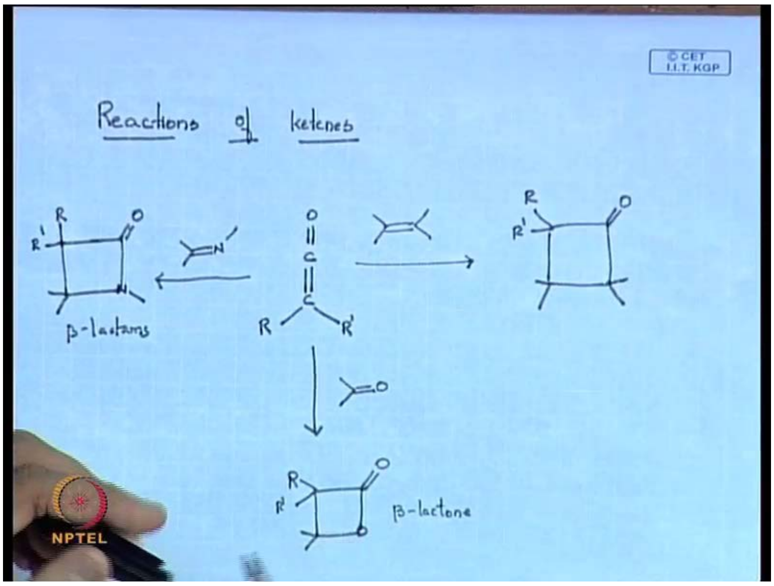

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See the n number of reactions, but we are going to concentrate with more which is 2 plus 2 cycloaddition. We are concerned more about 2 plus 2 cycloaddition reactions. For example, if we have a ketene like system like a general ketene. If I treat with an alkene, so it undergoes a type of 2 plus 2 cycloaddition. We will get in detail for other chemistry. Just we summarize. It is a type of summary of your ketenes what ketene can do and then, we will get into individual chemistry.

So, you end up with a product like ketone and this is your ketene part, right and then, this should be your, we can talk about this chemistry in detail, ok alkenes chemistry. Then, if you want to treat it with carbonyl compounds, what it would be with carbonyl compounds? You end up with your beta lacto. That also you can nice reactions. If you want to treat it with imine, then you get beta lactams, right. This is your famous Staudinger equation, right.

So, these all chemistry, these three chemistries happens in heating conditions. Now, we will go in detail and we will understand how these chemistry goes. We will first take alkenes, we will study them. Then, we will go to imine chemistry and then, we will go for carbonyl chemistry, ok. So, that is for this class. We will end our class right now with this.